

Transformation of 3-Chloroallyl Alcohol in Water-Saturated Subsoil Studied with a Column Method

Wim H. J. Beltman,* Minze Leistra & Arriënne M. Matser

DLO Winand Staring Centre for Integrated Land, Soil and Water Research (SC-DLO) PO Box 125, 6700 AC Wageningen, Netherlands

(Received 28 July 1995; revised version received 16 January 1996; accepted 22 February 1996)

Abstract: The performance of a newly developed column method for pesticide transformation rate measurements in the subsoil was tested using (Z)- and (E)-3-chloroallyl alcohol as model compounds. Sandy anaerobic water-saturated subsoil was collected at between 1.8 and 2.3 m below the surface of a flower-bulb field. Transformation rates were measured using subsoil columns that were filled *in situ* and were compared with the transformation rates in laboratory incubation systems. In the column experiment the half-life ranged from 0.5 to 5.2 days for (Z)-3-chloroallyl alcohol and from 1.0 to 5.5 days for (E)-3-chloroallyl alcohol. The capacity of the saturated subsoil for transformation of both isomers increased in the course of the column experiment. In the incubation experiment the 3-chloroallyl alcohols were transformed gradually in the first three days, with a half-life of 1.9 days for both isomers. Thereafter the transformation rate accelerated. The general conclusion is that the column method yields results similar to those of the incubation method for these rapidly transforming compounds.

Key words: groundwater, aquifer, 3-chloroallyl alcohol, column, transformation

1 INTRODUCTION

Predicting risks of agricultural pesticide use for the quality of groundwater is necessary, because groundwater is a major source of our drinking water. Several pesticides have been found in the upper groundwater in Western Europe¹ and the USA.² Other pesticides are expected to leach according to model simulations based on their physicochemical properties.^{3,4}

Models are used to simulate pesticide transport to drinking water wells. The results of model simulations are very sensitive to some of the main input parameters, including the half-life of the pesticide.⁵ It is therefore crucial to have a good estimate of the half-life of pesti-

cides in aquifers. Measuring half-lives in topsoils is difficult and it is even more difficult in aquifers,^{6,7} because of low microbial activity, low concentrations and anaerobic conditions in the aquifer. Half-lives are usually measured by means of laboratory incubation tests. This static method may not be representative for the conditions in the aquifer. Column methods to measure transformation of xenobiotics have been developed to simulate the dynamic field situation in the aquifer.^{8,9} In a column test, intensive contact between pesticide residues and reactive sites (e.g. micro-organisms) is provided by continuous water flow, in contrast to incubations, in which contact largely depends on diffusion. Nordmeyer *et al.* measured half-lives of pesticides in columns that were filled with aquifer material in the laboratory.¹⁰

* To whom correspondence should be addressed.

The 3-chloroallyl alcohols were used in this study because they are transformed at a reasonable rate,¹¹ which meant that results with the column test would be easy to obtain. The 3-chloroallyl alcohols are the main transformation products of (*Z*)- and (*E*)-1,3-dichloropropene in the soil.^{12,13} The soil fumigant 1,3-dichloropropene is a widely used nematicide in potato and flower-bulb crops in the Netherlands. Many fields with flower bulbs are situated within the groundwater extraction areas near the coastal dunes.

A column test was developed with columns filled in the field, disturbing the subsoil as little as possible.¹⁴ To test the method, the transformation rate of (*Z*)- and (*E*)-3-chloroallyl alcohol was measured. The aim of the experiment was to identify possible problems and to further optimize the method. The results of our column method were compared with those from the laboratory incubation method.

2 MATERIALS AND METHODS

2.1 Field description and subsoil collection

Subsoil material was collected from a flower-bulb field near Wassenaar (Province of South-Holland), close to the coastal dunes. The sandy water-saturated subsoil was collected from a depth of between 1.8 and 2.3 m below the soil surface. The water table was 1.5 m below the soil surface at the time of sampling (February 1993). The subsoil was a moderately coarse sand with 2% clay and silt fraction, no organic matter and 3% calcium carbonate.

The subsoil material was collected in stainless steel cylinders with a length of 360 mm and an inside diameter of 61 mm. They were fitted tightly inside one end of the cylinder holder and the top end of the holder was connected to a vacuum system. Another cylinder, with a length of 100 mm and an inside diameter of 61 mm, was taped to the lower end of the main cylinder.

The cylinders were filled *in situ* with material from the water-saturated zone. For this purpose, five holes were augered, at about 0.5 m from each other in a row. When the groundwater table was reached, PVC casing tubes (2 m long, outer diameter 90 mm, inner diameter 82 mm) were placed in the holes. The holes were deepened to 1.8 m by augering and baling, without additional water. The whole sampling system was connected to auger rods and then lowered into the hole, as shown in Fig. 1. The cylinder was purged with nitrogen gas before it was pressed into the subsoil. Then the nitrogen pressure was switched into vacuum. Pushing the extension rods down and pumping the air out of the holder made the cylinder move down into the saturated zone, thus filling it with subsoil. When the cylinder was filled,

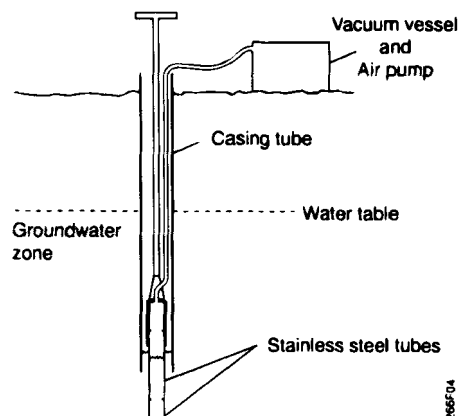


Fig. 1. Filling of the cylinder in the field. The top of the cylinder is connected to the cylinder holder. An extra 10-cm cylinder is connected to the lower end of the cylinder. The whole sampling system is lowered down inside the casing tube, down into the saturated subsoil.

the sampling system was pulled up to the soil surface while maintaining the vacuum in the cylinder holder. The cylinder system was disconnected from the auger rods and turned upside down. The extra 100-mm cylinder at the lower end was removed carefully. The top 5 mm of saturated material inside the cylinder was removed with a knife and replaced by a glass filter disc (pore size 100–160 μm), which disc prevented the saturated material from flowing out of the cylinder during the column test. Teflon tape was wrapped around the outer rim of the cylinder and a stainless steel cover was fixed over its top. The cover contained a small opening with a connection tube, allowing the water to be pumped through the tube in the column test. The cylinder was turned upside down and the cylinder holder was disconnected. Then a filter disc and a cover piece with connection tube were fitted onto this end of the column as well. The cover pieces were screwed firmly onto the cylinder to seal the column.

This procedure was repeated with the other four cylinders, after which the filled cylinders were placed in an isolation box to reduce temperature fluctuations in the subsoil during transport to the laboratory. Groundwater was pumped up from one of the bore holes with a vacuum pump, filling two 15-dm³ vessels to the top.

Subsoil for incubation experiments was collected afterwards from three of the bore holes. Equal amounts of subsoil were collected from each of the holes, using a vacuum column system as described by Leistra *et al.*¹¹ The subsoil was collected in a 15-dm³ polyethylene vessel, which was filled to the top with the saturated material. Subsoil and groundwater were stored in the dark during transport and in the laboratory. The temperature in the subsoil was 6.5°C at the time the field work was performed.

The pH value was measured with a TA-pH/T electrode, which was inserted into the holes. The electrode was connected to a WTW microprocessor pH-meter

(pH 196T) which was read after 5 min. The redox potential and the temperature were measured with a TA-pH/T redox electrode connected to the same micro-processor, which was read after 30 min.

2.2 Column experiment

The set-up of the column test is shown in Fig. 2. The groundwater was filtered through a 0.45- μm filter (Millipore) to remove bacteria, before it was put into the glass supply flask (10 dm³). Nitrogen gas was flushed continuously through the groundwater in the supply flask to keep the water anaerobic. The perfusion pump (Gilson Minipuls 2) forced the groundwater through the system. The PVC-tubes used in this pump were replaced regularly, because they wore out during pumping. At 48 h after the start of pumping, a concentrated solution of 3-chloroallyl alcohol was added to the groundwater flow using gastight glass syringes, at an injection rate determined by the infusion pump (Harvard Apparatus, Pump 22). Influent and effluent of the subsoil columns were sampled. All tubing and valves between the infusion pump and the effluent tube were stainless steel HPLC-tubing and valves. The column test was performed in a constant-temperature cabinet at 10°C.

The flow rate was adjusted to 0.400 dm³ day⁻¹ in the first 48 h before 3-chloroallyl alcohol was added to the groundwater. The experiment was divided into four periods with different values of groundwater flow rate and/or influent concentration. In the first period a flow rate of 0.400 dm³ day⁻¹ was used, equivalent to about one pore volume per day. The input concentration had to be low for a realistic simulation of aquifer conditions, but had to be high enough to detect substantial transformation, so a value of 500 $\mu\text{g dm}^{-3}$ was selected. For the second period the flow rate was reduced to 0.200 dm³ day⁻¹ to attain an effluent concentration of about half the influent concentration. After a steady state had been established the third period was started

where the input concentration was increased to 2500 $\mu\text{g dm}^{-3}$ by increasing the concentration in the syringe and by increasing the rate of injection by the infusion pump. In the fourth period the input concentration was reduced to the original value of 500 $\mu\text{g dm}^{-3}$ to verify whether the transformation capacity of the column had changed. The transformation rate was derived from the difference between the input concentration and the effluent concentration.

Two columns were installed in the test system (Fig. 2). The pore volumes of water in the columns after the test were measured. The columns were emptied and air-dried for 20 h at 105°C; they were weighed before and after drying. The pore volume was calculated from the volume of the columns (1.023 dm³) and the difference in mass after drying.

2.3 Incubation experiment

The incubation experiment was started one week after collecting the subsoil. A mass of about 300 g of water-saturated subsoil was weighed into glass flasks of 0.500 dm³ and 10 cm³ groundwater was added. The flasks were flushed with about 0.5 dm³ of nitrogen gas, closed with a glass stopper and placed in a constant temperature cabinet at 10°C. After seven days, 1 cm³ of an aqueous solution containing 15 mg dm⁻³ (Z)-3-chloroallyl alcohol and 15 mg dm⁻³ (E)-3-chloroallyl alcohol was added by slowly emptying the syringe while circling with its needle point at the bottom of the flask. The flask was flushed again with 0.5 dm³ of nitrogen gas. The glass stopper was wetted with distilled water when closing the flask, to prevent loss via the vapour phase. The flasks were gently swung round to obtain a good mixing of the 3-chloroallyl alcohol with the subsoil, and then incubated in the dark at 10°C.

Two incubation flasks were sampled every day, starting on the day when 3-chloroallyl alcohol was added. Fifteen minutes before sampling, the flasks were swung around as described above. A sample of 1 cm³ was taken from the water layer at the top of the subsoil. The samples were filtered through a 0.45- μm filter (Millex-HV) to remove solid material prior to analysis.

2.4 Analysis of (Z)- and (E)-3-chloroallyl alcohol

(Z)- and (E)-3-chloroallyl alcohol were measured by HPLC with UV-detection. Water samples were injected into a precolumn (100 \times 3 mm ID; C18, Chrompack). The mobile phase was acetonitrile + water (20 + 80 by volume), the flow rate was 0.5 cm³ min⁻¹ and the column temperature was 40°C. Just before the 3-chloroallyl alcohols eluted from the precolumn, it was

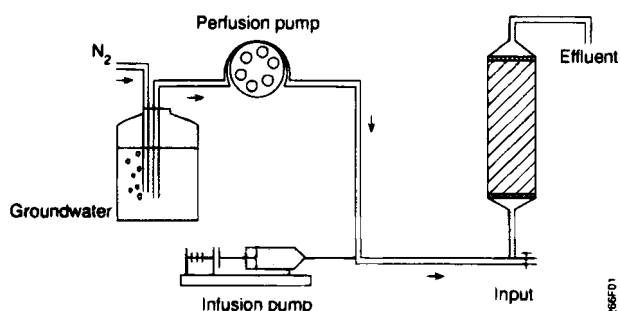


Fig. 2. Set-up of the column experiment. Groundwater is pumped through the column by the perfusion pump. The solution of 3-chloroallyl alcohol is added by means of the infusion pump.

connected to the analytical column (150x4 mm ID) filled with Lichrosorb 5-RP-18 (Merck). After the fraction with the 3-chloroallyl alcohols had entered the analytical column, the precolumn and the analytical column were disconnected. This procedure prevented interfering components from entering the analytical column. The 3-chloroallyl alcohols were detected with a LC90 UV-detector (Perkin Elmer) at 205 nm. The detection limit was $25 \mu\text{g dm}^{-3}$.

3 RESULTS AND DISCUSSION

3.1 Column experiment

The pH of the column effluent was measured at various times and was found to be 8.4. In the field the pH in the bore holes was 7.1, more than one pH unit lower. The increase was possibly caused by the flushing of the groundwater with nitrogen gas. The nitrogen bubbles may have stripped the carbon dioxide from the groundwater, resulting in a shift of the carbon dioxide-calcium equilibrium, which increases the pH.¹⁵

Redox potentials of -31 mV and $+15 \text{ mV}$ were measured after the experiment in the subsoils of Columns 1 and 2 respectively and matched well with the redox potentials measured in the field, which were in the range of 0 to 30 mV. A strong sulfurous smell noted while emptying the columns confirmed the anaerobic state of the aquifer material.

Sorption of 3-chloroallyl alcohol was not thought to be significant in the subsoil used because it contained no organic matter and as the breakthrough of the 3-chloroallyl alcohols took place after one pore volume of water had been pumped through the column it was justified to ignore sorption (see Fig. 3).

The concentrations of the (Z)- and (E)-3-chloroallyl alcohols measured in the influx and effluent of the columns are shown in Fig. 3. The flow rate and the intended input concentration in the four periods of the experiment are given in Table 1. Due to malfunctioning of the syringe plunger, some input concentrations were

not as intended. In these cases, the results were ignored in further analysis.

In the discussion that follows the concentrations in the influx and effluent of Column 1, for the (Z)-isomer and the (E)-isomer respectively are discussed first, followed by discussion on the concentrations in Column 2.

The concentrations of (Z)-3-chloroallyl alcohol in the influx of Column 1 (Fig. 3A) were close to the desired concentrations for each of the four periods (Table 1). In the first period, the effluent concentration of the (Z)-isomer was 0.64 times the input concentration (Figs 3A and 3B). In the second period, with the lower flow rate, the additional transformation in the column was less than expected. The much higher input concentration in the third period resulted in an effluent concentration of 0.71 times the input level. In the fourth period, some concentrations in the effluent dropped below the detection limit of $25 \mu\text{g dm}^{-3}$. Higher transformation rates occurred in the fourth period than in the second period, with the same flow rate and low input concentration.

The concentration of (E)-3-chloroallyl alcohol in the influx and effluent of Column 1 (Figs 3C and 3D) followed the same pattern as that of the (Z)-isomer. In the first two periods, the transformation rate of the (E)-isomer was higher than that of the (Z)-isomer. By contrast, the transformation rate in the fourth period was lower for the (E)-isomer. In the fourth period, the effluent concentration of the (E)-isomer did not drop as much as that of the (Z)-isomer; the concentrations of the (E)-isomer were all above the detection limit.

For Column 2, the input concentrations of (Z)-3-chloroallyl alcohol (Fig. 3E) were slightly higher than the intended concentrations. In the first period, the (Z)-isomer showed a lower transformation rate than in Column 1, its concentration decreasing only by a factor of 0.87. The measurements for the high input concentration in the third period varied greatly. In the fourth period there was a higher transformation rate in Column 2 compared to Column 1, but the effluent concentration did not drop below the detection level.

The concentration of (E)-3-chloroallyl alcohol in the influx and effluent of Column 2 (Figs 3G and 3H) followed the same pattern as the concentration of the (Z)-isomer. In the first two periods, the transformation rate of the (E)-isomer was somewhat greater than that of the (Z)-isomer. In the next two periods the differences in transformation rate were smaller. In the fourth period the effluent concentration of the (E)-isomer did not drop as much as that of the (Z)-isomer. This was consistent with the behaviour of the isomers in Column 1.

The input concentrations (Figs 3A, C, E, G) fluctuated more strongly than the effluent concentrations (Figs 3B, D, F, H); this phenomenon was most distinct for Column 2 in the third period. The fluctuations can be attributed to incomplete mixing of the 3-chloroallyl alcohols after injection into the groundwater flow and before reaching the sample port of the influx. Generally,

TABLE 1
Measured Flow Rate of Groundwater through the Columns and Intended Input Concentration in the Four Periods

Period	Time (days)	Flow rate ($\text{dm}^3 \text{ day}^{-1}$)		Concentration ($\mu\text{g dm}^{-3}$)
		Column 1	Column 2	
1	0-3.1	0.382	0.395	500
2	3.1-8.0	0.200	0.196	500
3	8.0-13.9	0.194	0.200	2500
4	13.9-19.9	0.198	0.199	500

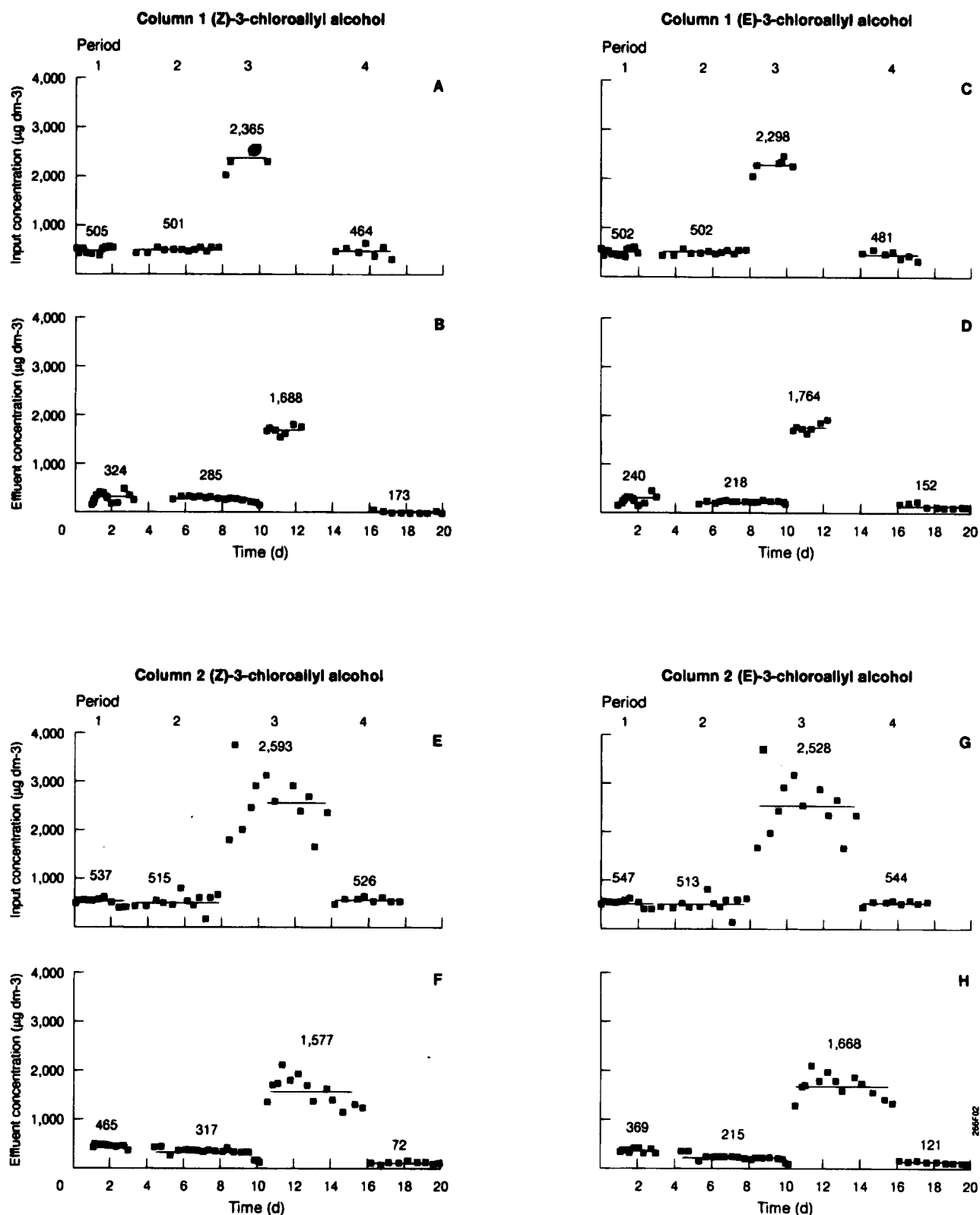


Fig. 3. Concentrations of (Z)- and (E)-3-chloroallyl alcohol measured in the influent and effluent of Columns 1 and 2. (A) (Z)-isomer in influent of Column 1, (B) (Z)-isomer in effluent of Column 1, (C) (E)-isomer in influent of Column 1, (D) (E)-isomer in effluent of Column 1, (E) (Z)-isomer in influent of Column 2, (F) (Z)-isomer in effluent of Column 2, (G) (E)-isomer in influent of Column 2, (H) (E)-isomer in effluent of Column 2. The average concentrations for each of the four periods are indicated by the horizontal lines, and their values are indicated above the lines. The periods 1 to 4, with different flow rates and influent concentrations (see Table 1), are indicated in the figures.

the fluctuations in the effluent concentration were less, due to further mixing in the water flow and due to hydrodynamic dispersion in the subsoil column.

For each period with steady-state conditions in the column experiment, the half-lives of (Z)- and (E)-3-chloroallyl alcohol were calculated. The results are given in Table 2. The half-life in the first period, with a comparatively high flow rate, shows a wide variation: it ranges from 1.0 to 5.2 days. The half-lives of the (Z)-isomer in period 1 were somewhat higher than those of the (E)-isomer.

Halving the flow rate increased the half-lives in Column 1 and decreased the half-lives in Column 2. The flow rate was only reduced to obtain a larger difference between the influx and the effluent concentration of the 3-chloroallyl alcohols, via a longer residence time in the columns. It was expected that the half-life of the compounds would not be affected by changes in the flow rate. In the first period, the half-lives in Column 2 were longer than those in Column 1, especially that of the (Z)-isomer. In the second period, the differences in half-life were much smaller. In the beginning microbial acclimatisation may have been better in Column 1.

In the third period of the column experiment, the input concentration of the chloroallyl alcohols was five times as high as before. In three of the four combinations this resulted in distinctly longer half-lives (Table 2). Only for the (Z)-isomer in Column 2 did the half-life remain almost the same. There are two possible explanations for a longer half-life at a higher concentration. The number of micro-organisms and the related quantity of enzymes may have been a limiting factor in the transformation rate. Another possibility is that the higher concentration resulted in a certain inhibition of microbial and enzymatic activity. Ou¹⁶ found no toxic effects of 3-chloroallyl alcohol at dosages of 50 µg per gram topsoil. The number of micro-organisms in the subsoil is much lower than in the topsoil and the

subsoil microflora is possibly more sensitive because of the reduced availability of nutrients in the subsoil, and its more stable environmental conditions. The possible inhibition did not last long; the transformation rate increased immediately after the input concentration was decreased in the fourth period.

In the fourth period, the input concentration was reduced to the original level. This resulted in a strong decrease of the half-lives (Table 2). In three of the four combinations, the half-life was much shorter than in the first two periods, with the same input concentration. The exception was (E)-3-chloroallyl alcohol in Column 1, for which the half-life had been short from the beginning. The main tendency was for the half-lives to become shorter during the column experiment, presumably by adaptation of the micro-organisms to the chloroallyl alcohols. The recovery from the possible inhibition of the transformation by the high concentration in the third period was rather fast.

The differences in half-life of the (Z)-isomer for the lower input concentration were greater (factor 5) than those of the (E)-isomer (factor 2); transformation of the (Z)-isomer seems to be more affected by the microbial adaptation.

3.2 Incubation experiment

The redox potential in the incubated aquifer material ranged between 18 and 84 mV, which was only slightly higher than in the field. This means that the redox conditions in the flasks were representative of the field situation. The transfer of the subsoil material to the laboratory and the subsequent incubation had no distinct effect on the redox potential of the subsoil material. The pH in the aquifer material in the flasks was 8.3 (± 0.1), which is more than one unit higher than the pH measured in the field. The pH value in the flasks

TABLE 2
Half-Lives of (Z)- and (E)-3-Chloroallyl Alcohol in Column 1 (Pore Volume 40%) and Column 2 (Pore Volume 42%)

Period	Flow rate/ concentration level	Half-life (days) of	
		(Z)-3-chloroallyl alcohol	(E)-3-chloroallyl alcohol
Column 1			
1	High/low	1.7	1.0
2	Low/low	2.5	1.7
3	Low/high	4.3	5.5
4	Low/low	0.5	1.3
Column 2			
1	High/low	5.2	1.9
2	Low/low	3.1	1.7
3	Low/high	3.0	3.6
4	Low/low	0.8	1.0

represents the condition of CO_2 - CaCO_3 equilibrium under atmospheric CO_2 pressure.¹⁵ In the field there is probably more CO_2 in the groundwater than under atmospheric conditions, due to diffusion limitations. CO_2 probably dissipated during sampling and handling of the subsoil. Hence the equilibrium shifts towards CaCO_3 and the pH is lower in the field.

Figure 4 shows the fraction of 3-chloroallyl alcohol which remained in the flasks as a function of time. The initial concentrations in the incubation experiments were measured to be $480 \mu\text{g dm}^{-3}$ for the *Z*-isomer and $441 \mu\text{g dm}^{-3}$ for the *E*-isomer. Gradual transformation took place in the first three days. During the following days, the gradual transformation continued in some flasks, whereas in other flasks there was a rapid transformation of the remaining 3-chloroallyl alcohol. After six days no (*Z*)-3-chloroallyl alcohol was left in the flasks and less than 5% of the dose of (*E*)-3-chloroallyl alcohol was left. Linear regression on the fractions remaining at the first three sampling times resulted in transformation rates corresponding to a half-life of 1.9 days for both isomers of chloroallyl alcohol. The accelerated transformation indicates adaptation of the micro-organisms to the 3-chloroallyl alcohols, which corresponds with the observations for the columns.

4 GENERAL DISCUSSION AND CONCLUSIONS

The results of the column test we have developed were compared with those of the conventional incubation test. The redox potential was within the range of -31 to 84 mV in both tests. Concentrations of (*Z*)- and (*E*)-3-chloroallyl alcohol were between $250 \mu\text{g dm}^{-3}$ and $500 \mu\text{g dm}^{-3}$ for three of the four periods in the column test and for the first two days of the incubation experi-

ment. Hence the half-lives of the column test and the half-lives of the first period in the incubation test can be compared. The half-lives were in the same range: between 0.5 and 5.5 days in the column test and 1.9 days in the incubation test. We conclude that the technical set-up of the column test is appropriate for measuring half-lives of rapidly transforming pesticides.

The transformation rate of the 3-chloroallyl alcohols increased in the course of both tests, probably because of microbial adaptation. The increase in transformation rate may be due to growth of the microbial population. Limiting conditions may have inhibited a faster growth of the microbial population. The set-up of the column experiment could have been used to study adaptation of the subsoil to 3-chloroallyl alcohol in more detail if we had kept the conditions at steady state.

In some earlier incubation experiments with water-saturated sandy subsoil from flower-bulb fields, Leistra *et al.*¹¹ measured longer half-lives. For (*Z*)-3-chloroallyl alcohol they found a half-life of 11 days for one subsoil, but half-lives ranged from 11 to 60 days for two other soils with a very large variation in duplicates. For (*E*)-3-chloroallyl alcohol they measured a half-life of about 12 days, after which there was a relatively rapid transformation of the remaining (*E*)-3-chloroallyl alcohol. All incubations were done in a similar way, at 10°C , in the dark. The redox potential in our incubations ranged from 18 to 84 mV, and in our columns from -31 to 15 mV, while the redox potential in their incubations was in the range of 250 to 370 mV. Redox potentials indicate which electron acceptor may be dominant in the system. The activity and occurrence of major microbial groups often depend largely on the available electron acceptor.^{9,17} The difference in transformation rates between the two studies may be related to the difference in redox conditions. Measuring redox conditions in

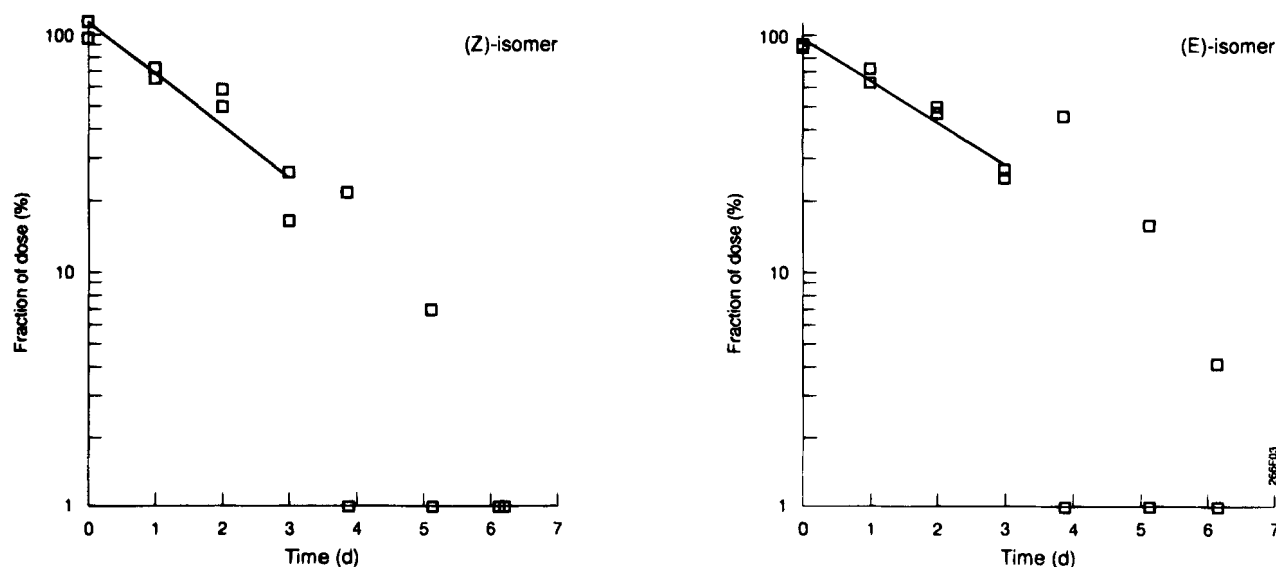


Fig. 4. Remaining fractions of (a) (*Z*)-3-chloroallyl alcohol and (b) (*E*)-3-chloroallyl alcohol in the subsoil material as a function of incubation time. The lines are linear regression approximations assuming first-order kinetics.

transformation studies with subsoil is of great importance. It is worthwhile to give further attention in research to the relation between redox condition and the transformation rate of pesticides.

An important reason for developing the column test was that it enables the measurement of transformation under different experimental conditions, by changing the flow rate in the column and the input concentration or the composition of the groundwater that is pumped through the column. These kinds of change are difficult to realize in incubation tests. The present set-up provided adequate opportunities to change flow rates and input concentrations, achieving the aim of allowing conditions for transformation to be changed in column tests.

An advantage of column tests over incubation tests is that the former are more representative of the field situation than the latter. However, column tests are time-consuming and the number of analyses is much larger than for the incubation tests, which could be a good reason to use incubation tests. The pH values and redox potentials in the incubations did not differ much from those in the columns. The half-lives that we measured for 3-chloroallyl alcohol were in the same range in both tests. This means that, as regards representativity for the field situation, the incubation test does not seem less valuable for 3-chloroallyl alcohol.

A disadvantage of the column test is that it is technically more complex and therefore more sensitive to technical problems than the relatively simple incubation test. The flow rate through the column has to be adapted to the expected transformation rate. The transformation rate should be large enough to measure differences between input and effluent concentrations, but small enough to provide a detectable effluent concentration. Pesticides that are transformed slowly need a low flow-rate in the column and the test should be continued over a long period of time.

With the current set-up, the column method has its limitations. The main threat to drinking water wells comes from more slowly transformed pesticide residues such as 1,2-dichloropropane, methyl isothiocyanate¹⁸ and atrazine.¹⁹ The transformation rates of these slowly transformed pesticides have been measured with the incubation method. Sometimes it takes years to quantify a transformation rate. Having shown that the column test is technically feasible, it can be adapted to measure transformation rates of slowly transformed pesticides. Instead of measuring the decline of the parent compound, the formation of transformation products could be measured. Then it is necessary to know the transformation products and/or to use radio-labelled pesticides. A column test can be successful if only a small percentage of detectable transformation products is formed within the travel time of the column. It seems worthwhile to maximize this travel time. However, this method is obstructed by the lack of

knowledge about the transformation products formed under anaerobic conditions.

The travel times of water to drinking water wells are of the order of years,⁵ whereas the half-lives in this study measured for the 3-chloroallyl alcohols were of the order of days. Hence, in the area from which the samples were taken, the risk of contamination of wells with 3-chloroallyl alcohols is minimal.

The general conclusion is that the column method yields results similar to those of the incubation method for these rapidly transforming compounds. We identified some major limitations of the column method, for which a solution needs to be found. Because of the need for representative methods for measuring transformation rates in the aquifer, it is worthwhile to further improve the column method.

ACKNOWLEDGEMENTS

We thank Geert-Jan Ankoné for his contribution to the experimental work and Leo van der Pas for assistance at the field work. The study was part of the Netherlands Integrated Soil Research Programme.

REFERENCES

1. Leistra, M. & Boesten, J. J. T. I., Pesticide contamination of groundwater in western Europe. *Agric. Ecosys. Environ.*, **26** (1989) 369–89.
2. Cohen, S., Results of the National Pesticide Survey. *Groundw. Monit.*, **11** (1991) 85–7.
3. Jury, W. A. & Gruber, J., A stochastic analysis of the influence of soil and climatic variability on the estimate of pesticide groundwater pollution potential. *Water Resour. Res.*, **25** (1989) 2465–74.
4. Boesten, J. J. T. I. & van der Linden, A. M. A., Modeling the influence of sorption and transformation on pesticide leaching and persistence. *J. Environ. Qual.*, **20** (1991) 425–35.
5. Beltman, W. H. J., Boesten, J. J. T. I. & van der Zee, S. E. A. T. M., Analytical modelling of pesticide transport from the soil surface to a drinking water well. *J. Hydrol.*, **169** (1995) 209–28.
6. Wilson, J. T., Smith, G. B., Cochran, J. W., Barker, J. F. & Roberts, P. V., Field evaluation of a simple microcosm simulating the behavior of volatile organic compounds in subsurface materials. *Water Resour. Res.*, **23** (1987) 1547–53.
7. Agertved, J., Rugge, K. & Barker, J. F., Transformation of the herbicides MCPP and atrazine under natural aquifer conditions. *Ground Water*, **30** (1992) 500–6.
8. Kuhn, E. P., van Loosdrecht, M., Giger, W. & Schwarzenbach, R. P., Microbial degradation of nitrilotriacetate (NTA) during river/groundwater infiltration: laboratory column studies. *Water Res.*, **21** (1987) 1237–48.
9. Heijman, C. G., Grieder, E., Holliger, C. & Schwarzenbach, R. P., Reduction of nitroaromatic compounds coupled to microbial iron reduction laboratory aquifer columns. *Environ. Sci. Technol.*, **29** (1995) 775–83.
10. Nordmeyer, H., Rose, H., Dibbern, H. & Pestemer, W., Pflanzenschutzmittel im Grundwasser—Säulenversuch

- unter anaeroben Bedingungen. *Wasser und Boden*, **2** (1991) 85–98.
11. Leistra, M., Groen, A. E., Crum, S. J. H. & van der Pas, L. J. T., Transformation rate of 1,3-dichloropropene and 3-chloroallyl alcohol in topsoil and subsoil material of flower-bulb fields. *Pestic. Sci.*, **31** (1991) 197–207.
 12. Castro, C. E. & Belser, N. O., Hydrolysis of *cis*- and *trans*-1,3-dichloropropene in wet soil. *J. Agric. Food Chem.*, **14** (1966) 69–70.
 13. Roberts, T. R. & Stoydin, G., The degradation of (*Z*)- and (*E*)-1,3-dichloropropenes and 1,2-dichloropropane in soil. *Pestic. Sci.*, **7** (1976) 325–35.
 14. Beltman, W. H. J., Hoogeweg, C. G. & Groen, A. E., A column test to study the biotransformation of pesticides in aquifers. In *Proc. Internat. Symp. Environ. Asp. Pestic. Microbiol.*, 17–21 August 1992, Sigtuna Sweden, ed. J.P.E. Anderson, D. J. Arnold, F. Lewis & L. Torstensson. Swedish University of Agricultural Sciences, Uppsala, Sweden, 1992, 318–24.
 15. Novozamsky I. & Beek, J., Common solubility equilibria in soil. In *Soil Chemistry. Part A: Basic Elements*, ed. G. H. Bolt & M. G. M. Bruggenwert. Elsevier Scientific Publishing Co., Amsterdam, 1976, pp. 96–125.
 16. Ou, L. T., Degradation of Telone II in contaminated and noncontaminated soils. *J. Environ. Sci. Health B*, **24** (1989) 661–74.
 17. Bosma, T. N. P., Cottaar, F. H. M., Posthumus, M. A., Teunis, C. J., van Veldhuizen, A., Schraa, G. & Zehnder, A. J. B., Comparison of reductive dechlorination of hexachloro-1,3-butadiene in Rhine sediment and model systems with hydroxocobalamin. *Environ. Sci. Technol.*, **28** (1994) 1124–8.
 18. Boesten, J. J. T. I., van der Pas, L. J. T., Smelt, J. H. & Leistra, M., Transformation rate of methyl isothiocyanate and 1,3-dichloropropene in water-saturated sandy subsoils. *Neth. J. Agric. Sci.*, **39** (1991) 179–90.
 19. Boesten, J. J. T. I. & van der Pas, L. J. T., Transformation rate of atrazine in water-saturated sandy subsoils. In *8th EWRS symposium "Quantitative approaches in weed and herbicide research and their practical application"*, Braunschweig, 1993, 381–7.